IV. "On the Superficial Viscosity of Water." By Lord Rayleigh, Sec. R.S. Received May 15, 1890.

The idea that liquids are endowed with a viscosity peculiar to the surface is to be found in the writings of Descartes and Rumford; but it is to Plateau that its general acceptance is due. His observations related to the behaviour of a compass needle, turning freely upon a point, and mounted in the centre of a cylindrical glass vessel of diameter not much more than sufficient to allow freedom of movement. By means of an external magnet the needle was deflected 90° from the magnetic meridian. When all had come to rest the magnet was suddenly removed, and the time occupied by the needle in recovering its position of equilibrium, or rather in traversing an arc of 85°, was noted. The circumstances were varied in two ways: first, by a change of liquid, *e.g.*, from water to alcohol; and, secondly, by an alteration in the level of the liquid relatively to the needle. With each liquid observations were made, both when the needle rested on the surface, so as to be wetted only on the under side, and also when wholly immersed to a moderate depth. A comparison of the times required in the two cases revealed a remarkable dependence upon the nature of the liquid. With water, and most aqueous solutions, the time required upon the surface was about *double* of that in the interior; whereas, with liquids of Plateau's second category, alcohol, ether, oil of turpentine, &c., the time on the surface was about *half* of the time in the interior. Of liquids in the third category (from which bubbles may be blown), a solution of soap behaved in much the same manner as the distilled water of the first category. On the other hand, solutions of albumen, and notably of saponine, exercised at their surfaces an altogether abnormal resistance.

These experiments of Plateau undoubtedly establish a special property of the surfaces of liquids of the first and third categories; but the question remains open whether the peculiar action upon the needle is to be attributed to a viscosity in any way analogous to the ordinary internal viscosity which governs the flow through capillary tubes.

In two remarkable papers,* Marangoni attempts the solution of this problem, and arrives at the conclusion that Plateau's superficial viscosity may be explained as due to the operation of causes already recognised. In the case of water and other liquids of the first category, he regards the resistance experienced by the needle as

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* 'Nuovo Cimento,' Ser. 2, vol. 5–6, Apr., 1872; 'Nuovo Cimento,' Ser. 3, vol. 3, 1878.

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mainly the result of the deformation of the meniscuses developed at the contacts on the two sides with the liquid surface. This view does not appear to me to be sound; for a deformation of a meniscus due to inertia would not involve any dissipation of energy, nor permanent resistance to the movement. But the second suggestion of Marangoni is of great importance.

On various grounds the Italian physicist concludes that "many liquids, and especially those of Plateau's third category, are covered with a superficial pellicle; and that it is to this pellicle that they owe their great superficial viscosity." After the observations of Dupré* and myself,† supported as they are by the theory of Professor Willard Gibbs,‡ the existence of the superficial pellicle cannot be doubted; and its mode of action is thus explained by Marangoni§:—"The surface of a liquid, covered by a pellicle, possesses two superficial tensions; the first, which is the weaker and in constant action, is due to the pellicle; the second is in the latent state, and comes into operation only when the pellicle is ruptured. Since the latter tension exceeds the former, it follows that any force which tends to rupture the superficial pellicle upon a liquid encounters a resistance which increases with the difference of tensions between the liquid and the pellicle." In Plateau's experiment the advancing edge of the needle tends to concentrate the superficial contamination, and the retreating edge to attenuate it; the tension in front is thus inferior to the tension behind, and a force is called into operation tending to check the vibration. On a pure surface it is evident that nothing of this sort can occur, unless it be in a very subordinate degree as the result of difference of temperature.

There is an important distinction, discussed by Willard Gibbs, according as the contamination, to which is due the lowering of tension, is merely accidentally present upon the surface, or is derived from the body of the liquid under the normal operation of chemical and capillary forces. In the latter case, that, for example, of solutions of soap and of camphor, the changes of tension which follow an extension or contraction of the surface may be of very brief duration. After a time, dependent largely upon the amount of contaminating substance present in the body of the liquid, equilibrium is restored, and the normal tension is recovered. On the other hand, in the case of a surface of water contaminated with a film of insoluble grease, the changes of tension which accompany changes of area are of a permanent character.

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* 'Théorie Mécanique de la Chaleur,' Paris, 1869, p. 377.

† "On the Tension of Recently Formed Liquid Surfaces," 'Roy. Soc. Proc.,' vol. 47, 1890, p. 281 (*supra*).

‡ 'Connecticut Acad. Trans.,' vol. 3, Part II, 1877–78. In my former communication I overlooked Prof. Gibbs's very valuable discussion on this subject.

§ 'Nuovo Cimento,' vol. 5-6, 1871–72, p. 260 (May, 1872).

It is not perfectly clear how far Marangoni regarded his principle of surface elasticity as applicable to the explanation of Plateau's observations upon distilled water; but, at any rate, he applied it to the analogous problem of the effect of oil in calming ripples. It is unfortunate that this attempt at the solution of a long-standing riddle cannot be regarded as successful. He treats the surface of the sea in its normal condition as contaminated, and therefore elastic, and he supposes that, upon an elastic surface, the wind will operate efficiently. When oil is scattered upon the sea, a non-elastic surface of oil is substituted for the elastic surface of the sea, and upon this the wind acts too locally to generate waves. It is doubtless true that an excess of oil may render a water surface again inelastic; but I conceive that the real explanation of the phenomenon is to be found by a precisely opposite application of Marangoni's principle, as in the theories of Reynolds* and Aitken.† Marangoni was, perhaps, insufficiently alive to the importance of *varying degrees* of contamination. An ordinary water surface is indeed more or less contaminated; and on that account is the less, and not the more, easily agitated by wind. The effect of a special oiling is, in general, to increase the contamination and the elasticity dependent thereupon, and stops short of the point at which, on account of saturation, elasticity would again disappear. The more elastic surface refuses to submit itself to the local variations of area required for the transmission of waves in a normal manner. It behaves rather as a flexible but inextensible membrane would do, and, by its drag upon the water underneath, hampers the free production and propagation of waves.

The question whether the effects observed by Plateau upon the surface of distilled water are, or are not, due to contamination must, I suppose, be regarded as still undecided. Oberbeck, who has experimented on the lines of Plateau, thus sums up his discussion:—"Wir müssen daher schliessen, entweder, dass der freien Wasseroberfläche ein recht bedeutender Oberflächenwiderstand zukommt, oder dass eine reine Wasseroberfläche in Berührung mit der Luft überhaupt nicht existirt."‡

Postponing for the moment the question of the origin of "superficial viscosity," let us consider its character. A liquid surface is capable of two kinds of deformation, dilatation (positive or negative) and shearing; and the question at once presents itself, is it the former or the latter which evokes the special resistance? Towards the answer of this question Marangoni himself made an important contribution in the earlier of the memoirs cited. He found (p. 245) that the substitution for the elongated needle of Plateau of a circular disc of thin brass turning upon its centre almost obliterated the distinction between liquids of the two first categories. The ratio of the superficial to the internal viscosity was now even greater for ether than for water. From this we may infer that the special superficial viscosity of water is not called into play by the motions of the surface due to the rotation of the disc, which are obviously of the nature of shearing.

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* 'Brit. Assoc. Rep.,' 1880.

† 'Edinburgh Roy. Soc. Proc.,' 1882-83, vol. 12, p. 56.

‡ Wiedemann's 'Annalen,' vol. 11, 1880, p. 650.

A varied form of this experiment is still more significant. I have reduced the metal in contact with the water surface to a simple (2″) ring ACBD of thin brass wire (fig. 1). This is supported by a fine silk fibre, so that it may turn freely about its centre. To give a definite set, and to facilitate forced displacements, a magnetised sewing needle, NS, is attached with the aid of wax. In order to make an experiment, the ring is adjusted to the surface of water contained in a shallow vessel. When all is at rest, the surface is dusted over with a little fine sulphur,* and the suspended system is suddenly set into rotation by an external magnet. The result is very distinct, and contrasts strongly with that observed by Plateau. Instead of the surface enclosed by the ring being carried round with it in its rotation, not the smallest movement can be perceived, except perhaps in the immediate neighbourhood of the wire itself. It is clear that an ordinary water surface does not appreciably resist shearing.

Fig 1.

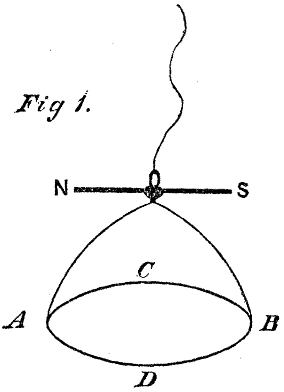
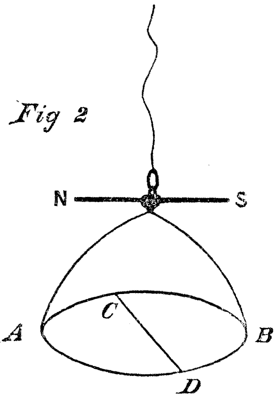


Fig 2



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* Sulphur seems to be on the whole the best material, although it certainly communicates some impurity to the surface. Freshly heated pumice or wood-ashes sink immediately; and probably all powders really free from grease would behave in like manner.

A very slight modification of the apparatus restores the similarity to that of Plateau. This consists merely in the addition to the ring of a material diameter of the same brass wire, CD, fig. 2. If the experiment be repeated, the sulphur indicates that the whole water surface included within the semicircles now shares in the motion. In general terms the surface may be said to be carried round with the ring, although the motion is not that of a rigid body.

Experiments of this kind prove that what a water surface resists is not shearing, but local expansions and contractions of area, even under the condition that the total area shall remain unchanged. And this is precisely what should be expected, if the cause of the viscosity were a surface contamination. A shearing movement does not introduce any variation in the density of the contamination, and therefore does not bring Marangoni's principle into play. Under these circumstances there is no resistance.

It remains to consider liquids of the third category in Plateau's nomenclature. The addition of a little oleate of soda does not alter the behaviour of water, at least if the surface be tolerably fresh. On the other hand, a very small quantity of saponine suffices to render the surface almost rigid. In the experiment with the simple ring the whole interior surface is carried round as if rigidly attached. A similar effect is produced by gelatine, though in a less marked degree.

In the case of saponine, therefore, it must be fully admitted that there is a superficial viscosity not to be accounted for on Marangoni's principle by the tendency of contamination to spread itself uniformly. It seems not improbable that the pellicle formed upon the surface may have the properties of a solid, rather than of a liquid. However, this may be, the fact is certain that a contracting saponine surface has no definite tension alike in all directions. A sufficient proof is to be found in the well known experiment in which a saponine bubble becomes wrinkled when the internal air is removed.

The quasi-solid pellicle on the surface of saponine would be of extreme thinness, and, even if it exist, could hardly be recognisable by ordinary methods of examination. It would moreover be capable of re-absorption into the body of liquid if unduly concentrated by contraction of surface, differing in this respect from the gross, and undoubtedly solid, pellicles which form on the surface of hard water on exposure to the atmosphere.

Two further observations relative to saponine may here find a place. The wrinkling of a bubble when the contained gas is exhausted occurs also in an atmosphere (of coal gas) from which oxygen and carbonic acid are excluded.

In Plateau's experiment a needle which is held stiffly upon the surface of a saponine solution is to a great extent released when the surface is contaminated by grease from the finger or by a minute drop of petroleum.

To return to the case of water, it is a question of the utmost importance to decide whether the superficial viscosity of even distilled water is, or is not, due to contamination with a film of foreign matter capable of lowering the tension. The experiments of Oberbeck would appear to render the former alternative very improbable; but, on the other hand, if the existence of the film be once admitted, the observed facts can be very readily explained. The question is thus reduced to this: Can we believe that the water surface in Plateau's apparatus is almost of necessity contaminated with a greasy film? The argument which originally weighed most with me, in favour of the affirmative answer is derived from the experiments of Quincke upon mercury. It is known that, contrary to all analogy, a drop of water does not ordinarily spread upon the surface of mercury. This is certainly due to contamination with a greasy film; for Professor Quincke* found that it was possible so to prepare mercury that water would spread upon it. But the precautions required are so elaborate that probably no one outside Professor Quincke's laboratory has ever witnessed what must nevertheless be regarded as the normal behaviour of these two bodies in presence of one another. The bearing of this upon the question under discussion is obvious. If it be so difficult to obtain a mercury surface which shall stand one test of purity, why may it not be equally difficult to prepare a water surface competent to pass another?

The method by which I have succeeded in proving that Plateau's superficial viscosity is really due to contamination consists in the preparation of a pure surface exhibiting quite different phenomena; and it was suggested to me by an experiment of Mr. Aitken.† This observer found that, if a gentle stream of air be directed vertically downwards upon the surface of water dusted over with fine powder, a place is cleared round the point of impact. It may be added that on the cessation of the wind the dust returns, showing that the tension of the bared spot exceeds that of the surrounding surface.

The apparatus, shown in figs. 3, 4, is constructed of sheet brass. The circular part, which may be called the *well*, has the dimensions given by Plateau. The diameter is 11 cm., and the depth 6 cm. The needle is 10 cm. long, 7 mm. in breadth at the centre, and about 0·3 mm. thick. It is suspended at a height of $2\frac{1}{2}$ cm. above the bottom of the vessel. So far there is nothing special; but in connexion with the well there is a rectangular trough, or tail-piece, about $2\frac{1}{2}$ cm. broad and 20 cm. long. Between the two parts a sliding door may

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* Poggendorff's 'Annalen,' vol. 139, 1870, p. 66.

† *Loc. cit.*, p. 69.

Fig 3.

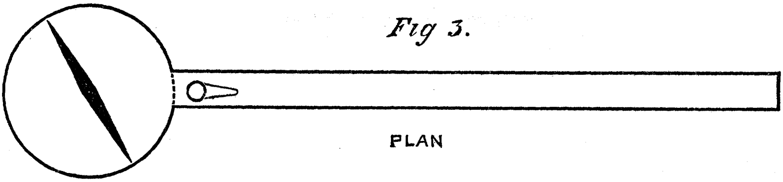
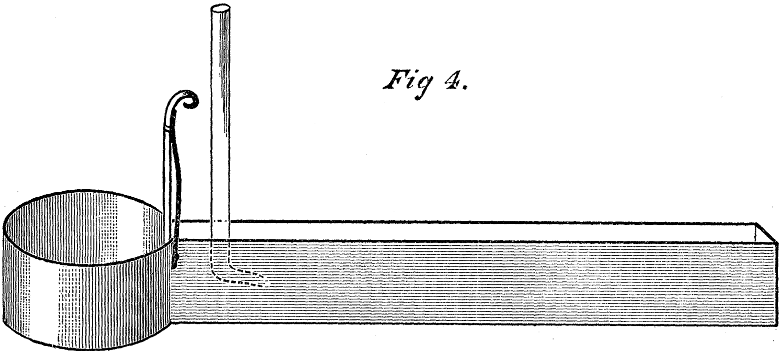


Fig 4.



Scale = $\frac{1}{5}$.

be inserted, by which the connexion is cut off, and the circular periphery of the well completed. The action of the apparatus depends upon a stream of wind, supplied from an acoustic bellows, and discharged from a glass nozzle, in a direction slightly downwards, so as to strike the water surface in the tail-piece at a point a little beyond the door. The effect of the wind is to carry any greasy film towards the far end, and thus to purify the near end of the tail-piece. When the door is up, this effect influences also the water surface in the well upon which the jet does not operate directly. For, if the tension there be sensibly less than that of the neighbouring surface in the tail-piece, an outward flow is generated, and persists as long as the difference of tensions is sensible. The movements of the surface are easily watched if a little sulphur be dusted over; when the water in the well has been so far cleansed that but little further movement is visible, the experiment may be repeated without changing the water by contaminating the surface with a little grease from the finger or otherwise. In this way the surface may be freed from an insoluble contamination any number of times, the accumulation of impurity at the far end of the tail-piece not interfering with the cleanness of the surface in the well.

Another device that I have usually employed facilitates, or at any rate hastens, the cleansing process. When the operation is nearly complete, the movement of the surface becomes sluggish on account of the approximate balance of tensions. At this stage the movement may be revived, and the purification accelerated, by the application of heat to the bottom of the well at the part furthest removed from the tail-piece. It may, perhaps, be thought that convection currents might be substituted altogether for wind; but in my experience it is not so. Until a high degree of purity is attained, the operation of convection currents does not extend to the surface, being resisted by the film according to Marangoni's principle.

When the apparatus was designed, it was hoped that the door could be made a sufficiently good fit to prevent the return of the greasy film into the well; but experience showed that this could not be relied upon. It was thus necessary to maintain the wind during the whole time of observation. The door was, however, useful in intercepting mechanical disturbance.

A very large number of consistent observations have been recorded. The return of the needle, after deflection to 90°, is timed over an arc of 60°, viz., from 90° to 30°, and is assisted by a fixed steel magnet acting in aid of the earth's magnetism. A metronome, beating three times per second, facilitates the time measurement. An an example, I may quote some observations made on April 11.

The apparatus was rinsed and carefully filled with distilled water. In this state the time was 12 (beats). After blowing for a while there was a reduction to 10, and after another operation to 8. The assistance of convection currents was then appealed to, and the time fell to $6\frac{3}{4}$, and after another operation to 6. This appeared to be the limit. The door was then opened, and the wind stopped, with the result that the time rose again to 12. More water was then poured in until the needle was drowned to the depth of about half an inch. Under these conditions the time was $6\frac{3}{4}$.

It will be seen, that while upon the unprepared surface the time was nearly twice as great as in the interior, upon the purified surface the time was somewhat less than in the interior.

For the sake of comparison, precisely similar observations were made upon the same day with substitution for water of methylated alcohol. Before the operation of wind the time was 5; after wind, 5; on repetition, still 5. Nor with the aid of convection currents could any reduction be effected. When the needle was drowned, the time rose to $7\frac{1}{4}$. The alcohol thus presents, as Plateau found, a great contrast with the unprepared water; but comparatively little with the water after treatment by wind and heat.

An even more delicate test than the time of vibration is afforded by the behaviour of the surface of the liquid towards the advancing edge of the needle. In order to observe this, it is necessary to have recourse to motes, but all superfluity should be avoided. In a good light it is often possible to see a few motes without any special dusting over. In my experience, an unprepared water surface always behaves in the manner described by Plateau; that is, it takes part in rotation of the needle, almost from the first moment. Under the action of wind a progressive change is observed. After a time the motes do not begin their movement until the needle has described a considerable arc. At the last stages of purification, a mote, situated upon a radius distant 30° or 40° from the initial direction of the needle, retains its position almost until struck; behaving, in fact, exactly as Plateau describes for the case of alcohol. I fancied, however, that I could detect a slight difference between alcohol and water even in the best condition, in favour of the former. With a little experience it was easy to predict the "time" from observations upon motes; and it appeared that the last degrees of purification told more upon the behaviour of the motes than upon the time of describing the arc of 60°. It is possible, however, that a different range from that adopted might have proved more favourable in this respect.

The special difficulties under which Plateau experimented are well known, and appealed strongly to the sympathies of his fellow workers; but it is not necessary to refer to them in order to explain the fact that the water surfaces that he employed were invariably contaminated. Guided by a knowledge of the facts, I have several times endeavoured to obtain a clean surface without the aid of wind, but have never seen the time less than 10. More often it is 12, 13, or 14. It is difficult to decide upon the source of the contamination. If we suppose that the greasy matter is dissolved, or, at any rate, suspended in the body of the liquid in a fine state of subdivision, it is rather difficult to understand the comparative permanence of the cleansed surfaces. In the case of distilled water, the condition will usually remain without material change for several minutes. On the other hand, with tap water (from an open cistern), which I have often used, although there is no difficulty in getting a clean surface, there is usually a more rapid deterioration on standing. The progressive diminution of the tension of well-protected water surfaces observed by Quincke* is most readily explained by the gradual formation of a greasy layer composed of matter supplied from the interior, and present only in minute quantity; although this view did not apparently commend itself to Quincke himself. If we reject the supposition that the greasy layer is evolved from the interior of the liquid, we must admit that the originally clean free surface, formed as the liquid issues from a tap, is practically certain to receive contamination from the solid bodies with which it comes into contact. The view, put forward hypothetically by Oberbeck, that contamination is almost instantly received from the atmosphere is inconsistent with the facts already mentioned.

Some further observations, made in the hope of elucidating this question, may here be recorded. First, as to the effect of soap, or rather oleate of soda. A surface of distilled water was prepared by wind and heat until the time was $5\frac{1}{2}$, indicating a high degree of purity. The door being closed, so as to isolate the two parts of the surface, and the wind being maintained all the while, a few drops of solution of oleate were added to the water in the tail-piece. With the aid of gentle stirring, the oleate found its way, in a few minutes, under the door, and reached the surface of the water in the well. The time gradually rose to 13, 14, 15; and no subsequent treatment with wind and heat would reduce it again below 12. In this case there can be no doubt that the contamination comes from the interior, and is quickly renewed if necessary; not, however, so quickly that the tension is constant in spite of extension or the surface would be free from superficial viscosity.

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* Poggendorff's 'Annalen,' vol. 160, 1877, p. 580.

In like manner, the time upon the surface of camphorated distilled water could not be reduced below 10, and the behaviour of motes before the advancing needle was quite different to that observed upon a clean surface. A nearly saturated solution of chloride of sodium could not be freed from superficial viscosity; while, on the other hand, an addition of $\frac{1}{3}$ per cent. of alcohol did not modify the behaviour of distilled water.

The films of grease that may be made evident in Plateau's apparatus are attenuated in the highest degree. In a recent paper* I have estimated the thickness of films of olive oil competent to check the movements of camphor fragments as from one to two micro-millimetres; but these films are comparatively coarse. For example, there was never any difficulty in obtaining from tap-water surfaces upon which camphor was fully active without the aid of wind or special arrangements. I was naturally desirous of instituting a comparison between the quantities necessary to check camphor movements and the more minute ones which could be rendered manifest by Plateau's needle; but the problem is of no ordinary difficulty. A direct weighing of the contamination is out of the question, seeing that the quantity of oil required in the well of the apparatus, even to stop camphor, would be only $\frac{1}{64}$ milligram.

The method that I have employed depends upon the preparation of an ethereal solution of olive oil, with which clean platinum surfaces are contaminated. It may he applied in two ways. Either we may rely upon the composition of the solution to calculate the weight of oil remaining upon the platinum after evaporation of the solvent, or we may determine the relative quantities of solution required to produce the two sorts of effects. In the latter case we are independent of the precise composition of the solution, and more especially of the question whether the ether may be regarded as originally free from dissolved oil of an involatile character. In practice, both methods have been used.

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* *Supra*, p. 364.

The results were not quite so regular as had been hoped, the difficulty appearing to be that the oil left by evaporation upon platinum was not completely transferred to the water surface when the platinum was immersed, even although the operation was performed slowly, and repeated two or three times. On the other hand, there was no difficulty in cleansing a large surface of platinum by ignition in the flame of a spirit lamp, so that it was absolutely without perceptible effect upon the movement of the needle over a purified water surface.

The first solution that was used contained 7 milligrams of oil in 50 c.c. of ether. The quantities of solution employed were reckoned in drops, taken under conditions favourable to uniformity, and of such dimensions that 100 drops measured 0·6 c.c. The following is an example of the results obtained :—On April 25, the apparatus was rinsed out and recharged with distilled water. Time = 13. After purification of surface by wind and heat, $5\frac{1}{2}$, rising, after a considerable interval, to 6. After insertion of a large plate of platinum, recently heated to redness, time unchanged. A narrow strip of platinum, upon which, after a previous ignition, three drops of the ethereal solution had been evaporated, was then immersed, with the result that the time was at once increased to $8\frac{1}{2}$. In subsequent trials two drops never failed to produce a distinct effect. Special experiments, in which the standard ether was tested after evaporation upon platinum, showed that nearly the whole of the effect was due to the oil purposely dissolved.

The determination of the number of drops necessary to check the movements of camphor upon the same surface seemed to be subject to a greater irregularity. In some trials 20 drops sufficed; while in others 40 or 50 drops were barely enough. There seems to be no doubt that the oil is left in a rather unfavourable condition,* very different from that of the compact drop upon the small platinum surface of former experiments; and the appearance of the platinum on withdrawal from the water often indicates that it is still greasy. Under these circumstances it is clearly the smaller number that should be adopted; but we are safe in saying that $\frac{1}{15}$ of the oil required to check camphor produces a perceptible effect upon the time in Plateau's experiment, and still more upon the behaviour of the surface before the advancing needle, as tested by observation of motes. At this rate the thickness at which superficial viscosity becomes sensible in Plateau's apparatus is about $\frac{1}{10}$ of a micro-millimetre, or about $\frac{1}{6000}$ of the wave-length of yellow light.

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* It should be stated that the evaporation of the ether, and of the dew which was often visible, was facilitated by the application of a gentle warmth.

A tolerably concordant result is obtained from a direct estimate of the smaller quantity of oil, combined with the former results for camphor, which were arrived at under more favourable conditions. The amount of oil in two drops of the solution is about 0·0017 milligram. This is the quantity which suffices to produce a visible effect upon the needle. On the large surface of water of the former experiments the oil required to check camphor was about 1 milligram. In order to allow for the difference in area, this must be reduced 64 times, or to 0·016 milligram. According to this estimate the ratio of thicknesses for the two classes of effects is about as 10 : 1.

Very similar results were obtained from experiments with an ethereal solution of double strength, one drop of which, evaporated as before, upon platinum, produced a distinct effect upon the time occupied by the needle in traversing the arc from 90° to 30°.

I had expected to find a higher ratio than these observations bring out between the thicknesses required for the two effects. The ratio 15 : 1 does not give any too much room for the surfaces of ordinary tap water, such as were used in the bath observations upon camphor, between the purified surfaces on the one side and those oiled surfaces upon the other, which do not permit the camphor movements.

It thus became of interest to inquire in what proportion the film originally present upon the water in the bath experiments requires to be concentrated in order to check the motion of camphor fragments. This information may be obtained, somewhat roughly it is true, by dusting over a patch of the water surface in the centre of the bath. When a weighed drop of oil is deposited in the patch, it drives the dust nearly to the edge, and the width of the annulus is a measure of the original impurity of the surface. When the deposited oil is about sufficient to check the camphor movements, we may infer that the original film bears to the camphor standard a ratio equal to that of the area of the annulus to the whole area of the bath. Observations of this kind indicated that a concentration of about six times would convert the original film into one upon which camphor would not freely rotate.

Another method by which this problem may be attacked depends upon the use of flexible solid boundary. This was made of thin sheet brass, and is deposited upon the bath in its expanded condition, so as to enclose a considerable area. Upon this surface camphor rotates, but the movement may be stopped by the approximation of the walls of the boundary. The results obtained by this method were of the same order of magnitude.

If these conclusions may be relied upon, it will follow that the initial film upon the water in the bath experiments is not a large multiple of that at which superficial viscosity tends to disappear. At the same time, the estimate of the total quantity of oil which must be placed upon a really pure surface in order to check the movements of camphor must be somewhat raised, say, from 1·6 to 1·9 micro-millimetre. It must be remembered, however, that on account of the want of definiteness in the effects, these estimates are necessarily somewhat vague. By a modification of Plateau's apparatus, or even in the manner of taking the observations, such as would increase the extent of surface from which the film might be accumulated before the advancing edge of the needle, it would doubtless be possible to render evident still more minute contaminations than that estimated above at one-tenth of a micro-millimetre.

[*Postscript, June* 4.—In order to interpret with safety the results obtained by Plateau, I thought it necessary to follow closely his experimental arrangements; but the leading features of the phenomenon may be well illustrated without any special apparatus. For this purpose, the needle of the former experiments may be mounted upon the surface of water contained to a depth of 1 or 2 inches in a large flat bath. Ordinary cleanliness being observed, the motes lying in the area swept over by the needle are found to behave much as described by Plateau. Moreover, the motion of the needle under the action of the magnet used to displace it is decidedly sluggish. In order to purify the surface, a hoop of thin sheet brass is placed in the bath, so as to isolate a part including the needle. The width of the hoop must of course exceed the depth of the water, and that to an extent sufficient to allow of manipulation without contact of the fingers with the water. If the hoop be deposited in its contracted state, and be then opened out, the surface contamination is diminished in the ratio of the areas. By this simple device there is no difficulty in obtaining a highly purified surface, upon which motes lie quiescent, almost until struck by the oscillating needle. In agreement with what has been stated above, an expansion of three or four times usually sufficed to convert the ordinary water surface into one upon which superficial viscosity was tending to disappear.

I propose to make determinations of the actual tensions of surfaces contaminated to various degrees; but in the meantime it is evident that the higher degrees of purity do not imply much change of tension. In the last experiment upon a tolerably pure surface, if we cause the needle to oscillate rapidly backwards and forwards through a somewhat large angle, we can clear away the contamination from a certain area. This contamination will of course tend to return, but observation of motes shows that the process is a rather slow one.

The smallness of the forces at work must be the explanation of the failure to clean the surface in Plateau's apparatus by mere expansion.

For this experiment the end wall was removed from the tail-piece (fig. 3), and a large flexible hoop substituted. By this means, it was hoped that when the whole was placed in the bath it would be possible, by mere expansion of the hoop, to obtain a clean surface in the well. The event proved, however, that the purification did not proceed readily beyond the earlier stages, unless the passage of the contamination through the long channel of the tail-piece was facilitated by wind.]

V. "Experiments with Lord Rayleigh's Colour Box." By ARTHUR SCHUSTER, F.R.S. Received May 15, 1890.

Lord Rayleigh described before the meeting of the British Association, in 1881,* a colour box in which artificial yellow is produced by mixing a pure red and green, and this yellow is directly compared to the yellow of the spectrum. Lord Rayleigh has given an account of certain peculiarities of vision observed in a number of persons, and it seemed to me worth while to extend the enquiry to a greater number of observers, and also, if possible, to obtain some evidence as to the existence of smaller differences than those described in Lord Rayleigh's paper.

The instrument used was made according to Lord Rayleigh's second pattern, in which a double-image prism is interposed between the slit and collimator lens; the prism which separates the light being a direct-vision prism. For the detailed description of the instrument I must refer the reader to Lord Rayleigh's paper.

My attention was in the first instance directed to prove or disprove the existence of small differences in different persons. It was necessary, therefore, only to take persons in whose observing powers I could place some reliance, and, secondly, to multiply the number of observations of each individual, so as to obtain an idea of the degree of accuracy to which the observations could be trusted. The instrument was used in a fairly dark room, and the observer was asked to place the Nicol so as to obtain the required match. After the reading had been taken the Nicol was displaced and the observations repeated. Five separate readings were thus generally obtained, and occasionally more. Often separate sets of observations were made for the right and left eye. As, owing to imperfections of construction, the zero of the instrument did not remain constant, either myself or Mr. Hadley, one of the demonstrators in the Phyisical Laboratory, took a reading whenever observations were made.

I have often compared my vision with Mr. Hadley's, and never detected any difference amounting to more than 0·1 of a division of the

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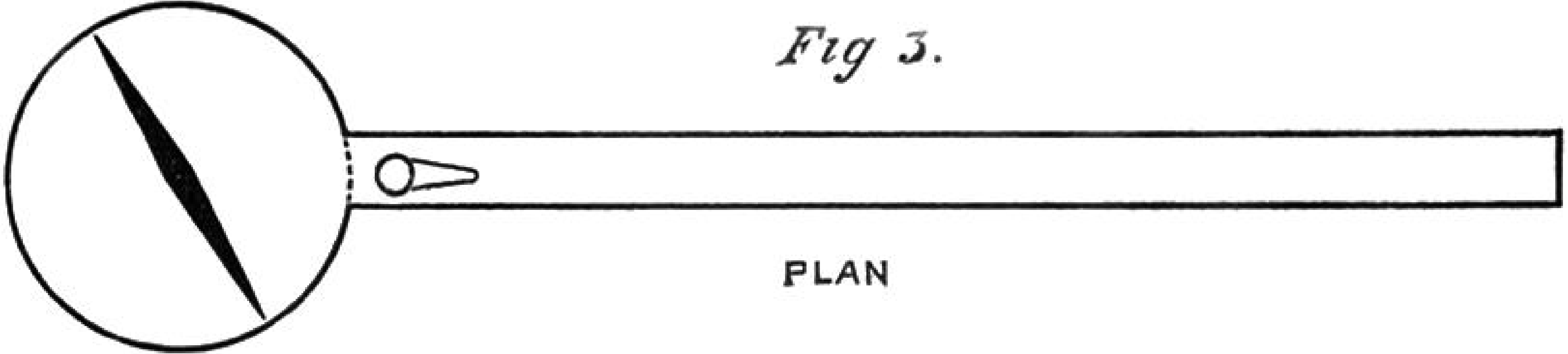
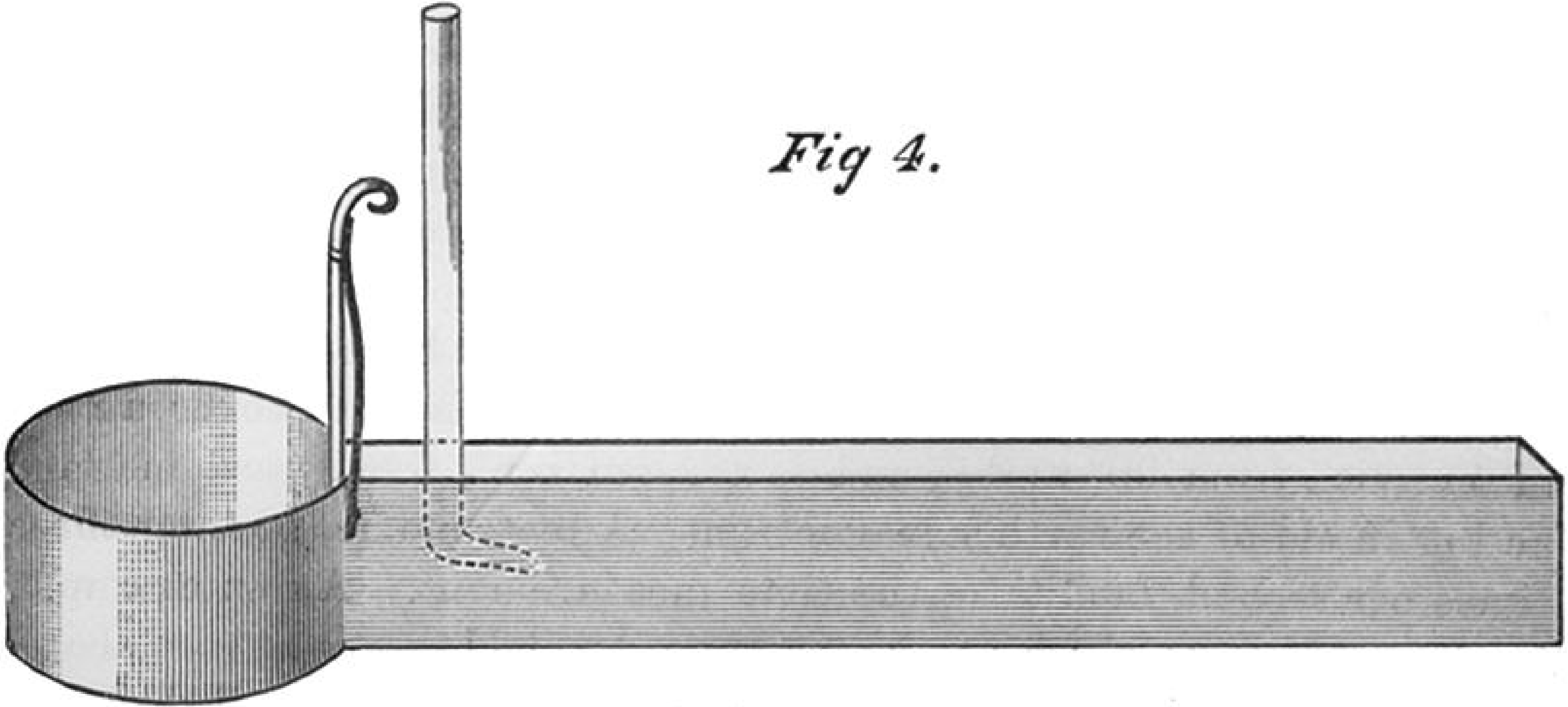
* 'Nature,' Nov. 17, 18 1.

Fig 3.



PLAN

Fig 4.



Scale = $\frac{1}{5}$.